# ASSOCIATION OF SOME ORGANIC ACIDS IN BENZENE SOLUTION

BY

FRED WENDALL BANES

B. Ed., Southern Illinois Normal University, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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## Introduction

The association of carboxylic acids in non-polar solvents was reported in 1888 by Beckmann as a result of cryoscopic and ebullioscope measurements[1, 2]. In 1891 Nernst[3] postulated the abnormal molecular weights obtained by studies of the distribution of certain carboxylic acids between water and non-polar solvents resulted from the association of the acid monomers into dimers in the organic solvent. Latimer and Rodebush[4] suggested that the association occurred as a result of hydrogen bonding between the two carboxyl groups. This theory of association has been studied and verified by a number of investigators [5, 6, 7, 8, 9].

Several methods of study of the association of carboxylic acids in solution have been used; these include freezing point depression[1, 10, 11, 12], boiling point elevation[13, 14], distribution coefficients[3, 15], electron diffraction[16], vapor density measurements[11, 17, 18], infra red absorption spectra[19, 20], and vapor lowering[21, 22, 23].

## Experimental and Results

The present investigation employs an indirect method of measuring vapor pressure lowering of solutions of benzoic acid, o-toluic acid, and m-toluic acid in benzene.

This method is essentially that of Barger[21] as modified by Signer[22], Lassettre and Dickinson[23], and later by Wall and Rouse[24], and depends on the isothermal distillation of a volatile solvent between an acid solution and a standard phenanthrene solution.

The apparatus consisted of two bulbs joined by a U-tube, with a graudated side arm sealed to each bulb at right angles to the U-tube. A solution of the acid to be studied was placed

in one bulb of the apparatus and a solution of phenanthrene in the other. The apparatus was then evacuated and placed in a thermostatic bath until the vapor pressures of the two solutions became equal. When this equilibrium had been attained, the volumes of the two solutions were read by tilting the apparatus so the solution flowed into the graduated side arms.

From the equilibrium volumes of the solutions, and the weight of their respective solutes, the concentrations of the solutions and the apparant molecular weights of the acid solutes were calculated. The concentrations of the solutions were obtained by the method of successive approximations, using equations for the density of the acid solutions given as a function of the temperature and concentration. The apparent molecular weights were used in turn to caluculate the degree of dissociation and the dissociation constant of the acid dimers at several temperatures and concentrations.

The heat of dissociation for each solute was calculated from the slope of the straight line obtained by plotting the common logarithm of the dissociation constant against the reciprocal of the absolute temperature. The equation of the straight line and the corresponding heat of dissociation of each solute is given in the following table:

| Solute | Equation | Heat of Dissociation of Dimer |
|---|---|---|
| Benzoic Acid | $\log_{10} K = 3.618 - 1919/T$ | $8780 \pm 260$ Cal. |
| m-Toluic Acid | $\log_{10} K = 4.056 - 2063/T$ | $9440 \pm 140$ Cal. |
| o-Toluic Acid | $\log_{10} K = 3.533 - 1836/T$ | $8400 \pm 140$ Cal. |

In the second table, given below, the probable error of the mean value of $\log_{10} K$ is given in column d. The next two columns give the percent error in the dissociation constant and in the common logarithm of this constant.

| Solute | d | % Error in K | % Error in $\log_{10}$ K |
|---|---|---|---|
| Benzoic Acid | 0.0085 | 1.96 | 0.350 |
| m-Toluic Acid | 0.0047 | 1.08 | 0.192 |
| o-Toluic Acid | 0.0041 | 0.94 | 0.181 |

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## VITA

The author was born at Raleigh, Illinois, on June 28, 1916. He received his elementary education in the public schools of Christopher, Illinois, and was graduated from the Christopher Community High School in June, 1934. He attended Southern Illinois Normal University at Carbondale, Illinois, from 1936 to 1940, receiving the degree of Bachelor of Education in June, 1940. The author attended the Graduate School of the University of Illinois from 1940 to 1943, holding a graduate assistantship in physical chemistry the first two years, and a University Fellowship the third year. He is a member of Sigma Xi, Phi Beta Kappa, Phi Lambda Upsilon, and Pi Mu Epsilon.

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